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AC and DC Electrical Conductivity Measurements on Glycine Family of Nonlinear Optical (NLO) Single Crystals

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Abstract

In the present work, the AC/DC conductivity studies were carried out on Glycine family of NLO single crystals such as Trisglycine Zinc Chloride (TGZC), Triglycine Acetate (TGAc) and Glycine Lithium Sulphate (GLS). The AC conductivity measurements were carried out using HIOKI 3532-50 LCR HITESTER in the frequency range of 50 Hz to 5 MHz for the grown NLO single crystals. The DC electrical conductivity measurements were also carried out for the crystals using the conventional two – probe technique in the temperature range of 313 – 423 K. The present study indicates that both the AC and DC conductivity of the samples increase with the increase in temperature. The activation energies were also calculated from AC/DC conductivity studies.

Keywords AC conductivity, DC conductivity, Glycine family of NLO Single Crystal

I. Introduction

Extensive studies have been made on the synthesis and crystal growth of nonlinear optical (NLO) materials over the past decade because of their potential applications in the field of telecommunications, optical signal processing and optical switching [1]. Organic nonlinear optical materials are attracting a great deal of attention due to their potentially high nonlinearities and rapid response in the electro-optic effect compared to inorganic NLO materials. The development of optical devices such as photonic integrated circuitry depends strongly on the design of highly efficient NLO materials. Among such NLO materials, organic materials are known to be superior to their inorganic counterparts in terms of synthesis, crystal fabrication, potential to create large devices and much faster optical nonlinearities [2, 3]. Operation of electro-optic devices is based on the Pockel's effect, in which the change in the dielectric constant is a linear function of the applied field [4]. Microelectronics industry needs replacement of dielectric materials in multilevel interconnect structures with new low dielectric constant(εr) materials, as an interlayer dielectric (ILD) which surrounds and insulates interconnect wiring. Lowering the dielectric constant values of the ILD decreases the RC delay, lowers power consumptions, and reduces 'cross-talk' between nearby interconnects [5]. The electrical conduction in dielectrics is mainly a defect controlled process in the low temperature region. The presence of impurities and vacancies mainly determine the behaviour in this region. The energy needs to form the defect is much larger than the energy needed for its drift. The conductivity of the crystal in the higher temperature region is determined by the intrinsic defects caused due to the thermal fluctuations in the crystal [6]. The low temperature conduction region seems to be connected to the mobility of vacancies. If the probability of occupation of an interstitial is f, then the probability of finding a vacant neighbour site is (1–f). Even for very high concentrations, of the order of 10^{20} cm^{-3}, f does not exceed 10^{-2} so that in real cases with concentration of interstitials of the order of 10^{15}–10^{20} cm^{-3}, (1–f) » 1[7]. Electrical conductivity may be influenced by the proton transport within the framework of hydrogen bonds. The conductivity is associated with the incorporation of impurity into the crystal lattice (of impurities) and the formation of corresponding defects in ionic crystals [8-10]. The proton conduction may be accounted for the motion of protons accompanied by a D defect (excess of positive charge). Migration of these defects may only modify electric polarization and may not change the charge at an electrode. In the present investigation, the AC/DC conductivity studies were carried out on Glycine family of NLO single crystals such as Trisglycine Zinc Chloride (TGZC), Triglycine Acetate (TGAc), and Glycine Lithium Sulphate (GLS). The activation energies were also calculated from AC/DC conductivity studies.

II. Materials and Methods

The NLO single crystals were grown by slow evaporation technique. Growth, Single crystal X-ray diffraction, UV analysis, FTIR, SHG, Thermal and Mechanical analysis, and Photoconductivity studies have been reported earlier by Suresh et al [11-13]. The conductivity of the material depends on its overall characteristics such as chemical composition, purity and crystal structure. Measurements taken with continuous currents provide only total conductivity. However, simultaneous information on conductivity and on the material's electrode interface effects can be partially offset by impedance measurements. Impedance measurement is a flexible tool for electrical characterization of materials. The compacted pellet (diameter 8 mm) of the sample is dried at 100ºC for few hours. In the present study, electric ohmic contacts were made using air drying silver paint on the opposite faces. Electrical measurements were taken in the frequency range from 50 Hz to 5 MHz using HIOKI 3532 LCR HITESTER. The AC impedance measurements were taken in the thermal range of 313 to 423 K. A chromel-Alumel thermocouple was employed to record the sample temperature. A time interval 30 minutes was taken prior to thermal stabilization after each measuring temperature. All the measurements were carried out in atmospheric air.

2.1. AC CONDUCTIVITY STUDY

A capacitor when charged under AC voltage will have some loss current due to ohmic resistance or impedance by heat absorption. If Q be the charge in Coulomb due to a potential difference of V volts between two plates of a condenser of area, A, and inter-plate distance d, then AC conductivity (σ_{ac}) due to AC voltage is given by the relation

$$\sigma_{ac} = J / E \tag{1}$$

J is the current density and is the electric field strength vector. But the electric field vector, $\vec{E} = \vec{D}/\varepsilon$, where is the displacement field vector of the dipole charges and ε is the complex permittivity of the material. For a parallel plate capacitor, the electric field intensity ($\vec{E}$) is the ratio of potential difference between the plates of the capacitor and the inter-plate distance. i.e.

$$\vec{E} = V / d \tag{2}$$

The current density, where Q is given by

$$Q = V\varepsilon A / d$$

Therefore,

$$J = (1/A)dQ/dt = d/dt(V\varepsilon/d) = \varepsilon/d.dV/dt \tag{3}$$

$$J = (\varepsilon/d)dV/dt \tag{4}$$

Substituting for and J in (1)

$$\sigma_{ac} = J/\vec{E} = \varepsilon j\omega \tag{5}$$

where ε is a complex quantity

$$\sigma_{ac} = (\varepsilon' - j\varepsilon'')j\omega = \varepsilon' j\omega + \omega\varepsilon'' \tag{6}$$

In order that the AC conductivity may be a real quantity, the term containing j has to be neglected. Hence,

$$\sigma_{ac} = \omega\varepsilon'' \tag{7}$$

In any dielectric material, there will be power loss because of the work done to overcome the frictional damping forces encountered by the dipoles during their rotation. If AC field is considered, then in an ideal case the charging current I_C will be 90º out of phase with the voltage. But in most of the capacitors due to the absorption of electrical energy some loss current, I_L will also be produced, which will be in phase with the voltage. Charging current, I_C, and loss current, I_L, will make angles δ and θ, respectively with the total current (I), passing through the capacitor. The loss current is represented by sin δ with respect to the total current (I). Generally, sin δ is called the loss factor, but when δ is small then, sin δ = δ = tan δ. But the two components ε' and ε'' of the complex dielectric constant (ε,) will be frequency dependent and is given by

$$\varepsilon'(\omega) = D_0 \cos\delta / \vec{E}_0$$

$$\varepsilon''(\omega) = D_0 \sin\delta / \vec{E}_0 \tag{8}$$

Since the displacement vector in a time varying field will not be in phase with $\vec{E}$ there will be a phase difference δ between them. From (7) and (8), we have

$$\tan\delta = \varepsilon''(\omega)/\varepsilon'(\omega) \tag{9}$$

Substituting the value of (ω) from (6) and (9) we have

$$\sigma_{ac} = \omega \tan\delta\varepsilon'(\omega) \tag{10}$$

where ω = 2πf and $\varepsilon' = \varepsilon_0\varepsilon_r$, where ε_r is the relative permittivity of the material and ε_0 the permittivity of the free space. So

$$\sigma_{ac} = 2\pi f \tan\delta\varepsilon_0\varepsilon_r \tag{11}$$

This equation is used to calculate the AC conductivity using dielectric constant and tan δ at a given frequency. It is to be noted that both tan δ and εr were available from dielectric measurement. The plots between ln(σ_{ac}) and 1000/ T were found to be very linear. Hence, the conductivity values can be fitted to the relation

$$\sigma_{ac} = \sigma_0 \exp[-\vec{E}/kT] \tag{12}$$

Where is the activation energy, k, the Boltzmann constant, T, the absolute temperature and σ_0 the parameter depending on the material. Activation energy was estimated using the slopes of the above line plots [$\vec{E}$ = -(slope)k x1000].

2.2. DC CONDUCTIVITY STUDY

The DC conductivity of the grown crystals was measured using the two-probe technique. The samples (rectangular shaped crystals) were cut parallel to the cleavage plane to the desired thickness of 1-2 mm and polished using silicon carbide paper. They were annealed for two hours at 423 K to remove the resistance moisture content. Opposite faces of the crystals were coated with good quality graphite to obtain a good ohmic contact with the electrodes. The samples were again annealed in the holder assembly at 423 K before making observations. The resistance of the crystal was measured using a megohmmeter. The observations were made while cooling the sample and temperature was controlled to an accuracy of ± 1°C. The dimensions of the crystal were measured using a travelling microscope. The DC conductivity (σ_{dc}) of the crystal was calculated using the relation,

$$\sigma_{dc} = t / RA \tag{13}$$

where R is the measured resistance, t is the thickness of the sample and A is the area of the face in contact with the electrode. The above procedure was used to determine the DC electrical conductivity. The general relation for the temperature variation of conductivity is given by

$$\sigma_{dc} = \sigma_0 \exp\left[- E / kT\right] \tag{14}$$

where σ_0 is a constant depending on material, E is the activation energy, T the absolute temperature and k is the Boltzmann's constant. The above equation can be rewritten as

$$\ln \sigma_{dc} = \ln \sigma_0 - E / kT \tag{15}$$

A plot of $\ln\sigma_{dc}$ versus 1000/T gives - E/k as the slope and $\ln\sigma_{dc}$ as the intercept. It is customary to plot $\ln\sigma_{dc}$ versus 1000/T, from the slope of which activation energy (E) can be calculated.

III. Results and Discussion

3.1. AC conductivity studies

Dielectrics exhibit a combined conduction, especially ionic and electronic conduction. Ionic conductivity studies provide valuable information about the state of point imperfections. In the high temperature (intrinsic) region, the effect of impurity on electrical conduction will not change appreciably whereas in the low temperature (extrinsic) region the presence of impurity in the crystal increases its conductivity. The energy needed to form the defect is much larger than the energy needed for its drift. The conductivity of the crystal in the high temperature region is determined by the intrinsic defects caused by thermal fluctuations in the crystal. Conduction in an ionic crystal is, in general, a defect controlled property. The defect concentration increases exponentially with rise of temperature and the electrical conductivity increases correspondingly. The Arrhenius plot of log σ_{ac} versus 1000 / T is shown in Figs.1, 3, and 5. The activation energy for ionic migration was estimated from the graph. The plot of $\ln\sigma_{ac}$ versus 1/T obeys Arrhenius relationship $\sigma_{ac} = \sigma_0 \exp(- E_a / kT)$ where σ_0 is the pre-exponent factor, E_a activation energy for the conduction process and k is the Boltzmann constant. Therefore, the crystal exhibits Arrhenius type conductivity behaviour in the temperature range of investigation. The activation energy of TGZC, TGAc and GLS for the conduction process calculated from plots is found to be 0.035 eV, 0.075 eV and 0.10 eV. The electrical conduction is mainly a defect controlled process in low temperature region. It is observed that the electrical conduction of glycine family of crystals is low at low temperature owing to trapping of some carriers at defect sites. As temperature rises, more and more defects are created, and as a result, the conductivity increases, which is predominantly due to motion of defects produced by thermal activation.

3.2. DC Conductivity Studies

Electrical conductivity depends on thermal treatment of a crystal. Thus, the conductivity at low temperatures depends on the cooling rate from melting point to room temperature. Thus, for slow cooling, the remaking of the lattice can occur by the migration of interstitials to vacancies recombination of Schottky defects or migration of vacancies to the surface along dislocation channels. On quenching or rapid cooling, a fraction of the vacancies freeze and the pre exponential term includes a contribution from those frozen vacancies. The value of DC conductivity is found to increase with temperature. The activation energy (E_a) for temperatures range of 313 to 423 K has been calculated from the slope of the graph between $\ln\sigma_{dc}$ and 1/T (Figs. 2, 4 and 6). It is found to be 0.050 eV, 0.060 eV and 0.055 eV for the crystals TGZC, TGAc and GLS respectively. Evaluation of DC electrical conductivity reveals useful information about materials to exploit them for various applications. The study of DC electrical conductivity sheds light on the behaviour of charge carriers under a DC field, their mobility and mechanism of conduction. At any particular temperature, the Gibb's free energy of a crystal is minimum when a certain fraction of ions leave the normal lattice.

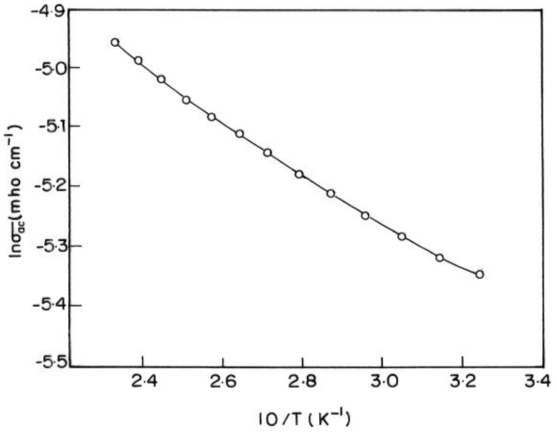

Figure 1. Plot of ln (σ_{ac}) versus 1000/T for TGZC single crystal

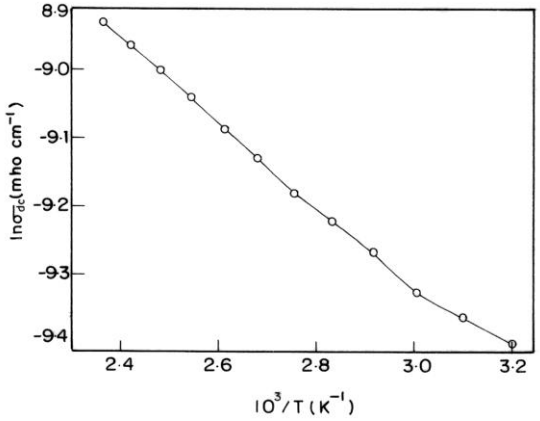

Figure 2. Plot of ln (σ_{dc}) versus 1000/T for TGZC single crystal

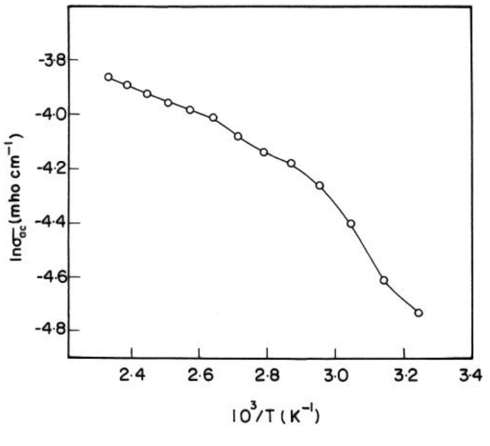

Figure 3. Plot of ln (σ_{ac}) versus 1000/T for TGAc single crystal

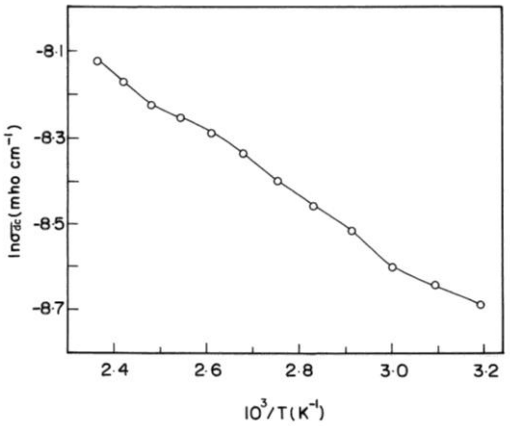

Figure 4. Plot of ln (σ_{dc}) versus 1000/T for TGAc single crystal

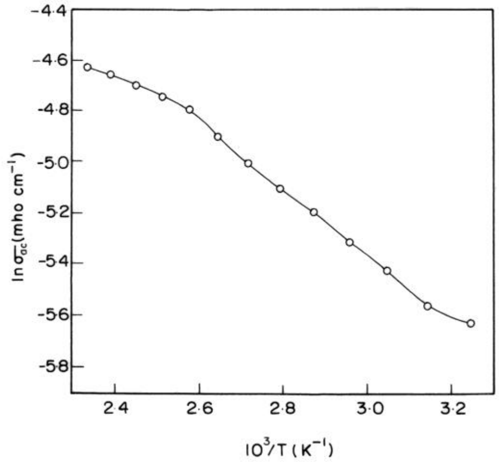

Figure 5. Plot of ln (σ_{ac}) versus 1000/T for GLS single crystal

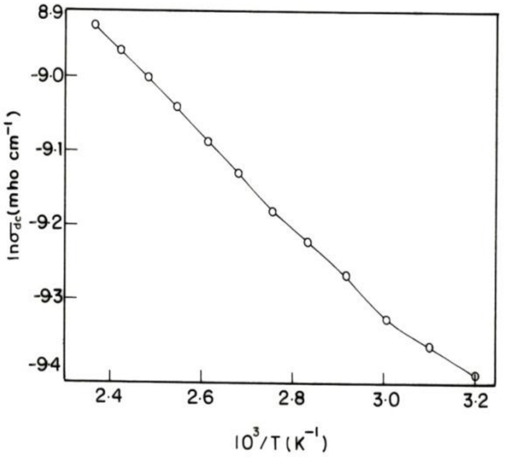

Figure 6. Plot of ln (σ_{dc}) T versus 1000/T for GLS single crystal

IV. Conclusion

Single crystals of Semi-organic nonlinear optical materials, such as Trisglycine Zinc Chloride (TGZC), Triglycine Acetate (TGAc), and Glycine Lithium Sulphate (GLS) have been grown by slow evaporation method. The AC/DC electrical conductivity studies were carried out on the grown single crystals. The AC electrical conductivity studies were carried out on the grown single crystals. The activation energy of TGZC, TGAc and GLS for the conduction process calculated from plots is found to be 0.035 eV, 0.075 eV and 0.10 eV. The activation energy for temperatures range of 313 to 423 K has been calculated from DC conductivity studies. It is found to be 0.050 eV, 0.060 eV and 0.055 eV for the crystals TGZC, TGAc and GLS respectively. The lower activation energies estimated from electrical conductivity studies suggests that the material contains less number of charge carriers for conduction process and the dielectric behaviour is very well understood.

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